

## The Kinetics of the Gas-phase Reactions of Selected Monoterpenes and Cyclo-alkenes with Ozone and the NO<sub>3</sub> Radical.

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The relative rate method has been used to measure the room-temperature rate constants for the gas-phase reactions of ozone and NO<sub>3</sub> with selected monoterpenes and cyclo-alkenes with structural similarities to monoterpenes. Measurements were carried out at  $298 \pm 2$  K and  $760 \pm 10$  Torr. The following rate constants (in units of  $10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were obtained for the reaction with ozone: methyl cyclohexene (132±15), terpinolene (1250±325), ethylidene cyclohexane (222±57), norbornene (959±249), t-butyl isopropylidene cyclohexane (1510±200), cyclopentene (546±61), cyclohexene (81.8±10.5), cyclooctene (454±45), dicyclopentadiene (1460±150) and  $\alpha$ -pinene (95.5±9.8). For the reaction with NO<sub>3</sub> the rate constants obtained (in units of  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were: methyl cyclohexene (7.91±0.76), terpinolene (46.9±5.1), ethylidene cyclohexane (4.39±0.30), norbornene (0.27±0.02), cyclohexene (0.54±0.02), cyclooctene (0.52±0.02), dicyclopentadiene (1.21±0.06) and  $\alpha$ -pinene (5.20±0.32). Molecular orbital energies were calculated for each alkene and the rate data are discussed in terms of the deviation from the structure-activity-relationship obtained from the rate constants for a series of simple alkenes. Lifetimes with respect to key initiators of atmospheric oxidation have been calculated suggesting that the studied reactions play dominant roles in the night-time removal of these compounds from the atmosphere.